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Short-Duration Autoignition Temperature Measurements for Hydrocarbon Fuels

Kermit C. Smyth and Nelson P. Bryner



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ABSTRACT

A new apparatus has been designed, built, and extensively tested for making short-duration autoignition temperature measurements of hydrocarbon fuels under conditions where the fuel/air stoichiometry, the nature of the hot metal surface, and the contact time are well controlled. This approach provides a much more reliable database to establish the importance of fuel structure effects than the current ASTM E659 procedure. Over 1100 individual autoignition temperature determinations have been made for the ignition of 15 hydrocarbon fuels on heated nickel, stainless steel, and titanium surfaces for three different fuel/air mixtures (stoichiometry $\phi = 0.7, 1.0, \text{ and } 1.3$). Excellent reproducibility has been achieved with the new apparatus.

The measured autoignition temperatures generally decrease for the larger hydrocarbons and for richer mixtures, with the C_2 hydrocarbons (ethane, ethylene, and acetylene) having particularly low values. The highest autoignition temperatures are observed for nickel surfaces and the lowest for stainless steel, with titanium being an intermediate case.

A review of the autoignition literature suggests that the branched alkanes should be more resistant to autoignition than the linear isomers, and thus present a reduced hazard. Limited data obtained in this study are consistent with this prediction. Promising directions for substantiating these observations and additional areas for future research are outlined.

SECTION I INTRODUCTION

A. OBJECTIVE

The autoignition of hydrocarbon fuels on hot surfaces is a process of practical significance which occurs when self-sustained combustion of a gas mixture is initiated. Possible prevention can be accomplished by choosing fuels of the proper molecular structure, by choosing the composition, coatings, or treatment of the hot surface, or by other intervention strategies. The goal of the present investigation is to devise a reliable method for measuring the autoignition behavior of hydrocarbon fuels in order to formulate appropriate strategies to reduce autoignition tendencies.

B. BACKGROUND

Self-ignition temperatures for hydrocarbon fuels depend on both the molecular structure of the fuel and on the surface material. However, the investigation of these effects is hampered by use of the standard ASTM E659 test procedure [1], which is based upon the 1954 apparatus of Setchkin [2]. In this method ignition often requires long times, as much as 10 minutes, without the capability of varying the material composition of the hot surface (borosilicate glass is the only surface used presently). The ASTM standard states that although liquids are commonly injected into the hot flask, "no condensed phase, liquid or solid, should be present when ignition occurs." Therefore, although this test attempts to measure the autoignition temperature of hydrocarbon fuels in the gas phase, for long-duration exposures of the fuels to the heated surface it is more likely that ignition temperatures for a complex mixture of the products of fuel decomposition are being determined rather than those of the original fuel. A method for measuring autoignition temperatures involving short times would greatly reduce the unknown extent of fuel decomposition and would provide more meaningful data on fuel structure and surface effects. Such measurements are also more relevant for determining hazards arising from malfunctions and accidents, where exposure times are short.

C. SCOPE/APPROACH

The scope of the present investigation involves (1) the development of experimental methods for the reliable determination of autoignition temperatures under a variety of conditions which involve short duration exposures of controlled fuel/air mixtures on various metal surfaces and (2) the interpretation of these data in terms of chemical mechanisms. Key issues include: (1) a comparison of ASTM test methods versus more controlled scientific tests for the determination of autoignition properties; and (2) the effects of surface materials, surface temperatures, and residence time upon autoignition temperatures of hydrocarbon fuels. The primary emphasis is on fuel structure effects, so that a reliable database can be established for testing the proposed mechanisms of autoignition.

In our apparatus a flowing gas-phase fuel stream impinges on a hot surface whose composition and temperature are controlled. Under these experimental conditions a large number of parameters can influence the measured autoignition temperature [3]. These include the following:

- fuel structure
- surface material
- surface temperature
- fuel/air stoichiometry

- surface size
- surface orientation
- initial fuel/air temperature
- contact or residence time (fuel/air velocity)
- condition of surface
- pressure
- heating rate of surface.

Our strategy was to vary the first four parameters systematically and to keep the remaining parameters fixed. In addition, the key role of stoichiometry needs to be examined, since autoignition temperatures can vary strongly with the fuel/air mixture ratio, especially for catalytic surfaces such as platinum [4-6]. To establish accurately the fuel structure effects upon ignition temperatures, three different stoichiometric conditions were investigated. This consideration required premixing of the fuel and air in known proportions. The conventional ASTM E659 procedure does not control the fuel/air stoichiometry.

Key features of the test apparatus include the following:

Short duration test - The contact time for the fuel/air mixture on the heated surface is less than 100 milliseconds. This short residence time avoids significant decomposition of the fuel and ensures that the ignition temperature measurement reflects more closely the ignition of the original fuel.

Surface Heating - The ignition surface is heated to 1200 °C in a uniform and controlled manner. The experimental approach allows multiple measurements to be made with excellent reproducibility.

Ignition criterion - The visual appearance of a burner-stabilized flame establishes a reproducible and reliable ignition criterion.

Premixed flame burner - This provides a straightforward means to vary the fuel/air stoichiometry easily and also prevent flashback after ignition has occurred. The flow of fuel and air can be shrouded in order to maintain the desired stoichiometry.

Open system - An open system avoids possible explosion hazards upon ignition and also provides access for mass spectrometric sampling and optical measurements should these become desirable in the future.

SECTION II
TEST METHOD FOR MEASURING SHORT DURATION AUTOIGNITION TEMPERATURES:
EXPERIMENTAL CONSIDERATIONS

An apparatus for measuring autoignition temperatures must be able to heat the ignition surface uniformly and reproducibly up to 1200 °C, introduce a specific fuel/air mixture onto the heated surface, and measure the time-temperature history of the surface during the ignition of the fuel. Design considerations include (1) the size of the ignition surface, (2) the orientation of the ignition surface, (3) the method for heating the surface, (4) the fuel delivery system for liquid and gaseous fuels, and (5) the technique for the measuring surface temperature.

A. IGNITION SURFACE SIZE

Keeping the heated area of the ignition surface small is desirable because this reduces the heating, time, fuel, and material requirements. A small surface can be heated more uniformly and quickly than a larger ignition area. Multiple ignitions for each surface and each fuel/air mixture are required, and thus time savings are realized using a small surface area which equilibrates at the desired temperature much faster than a larger surface. A small ignition area also does not require large quantities of the fuel/air mixture to ensure complete coverage of the heated ignition area. Providing high fuel flow rates for the light hydrocarbon fuels would not be a serious problem, since these fuels are readily available in high-pressure cylinders. However, for liquid fuels which must be vaporized using bubblers, only smaller fuel flow rates can be obtained without heating the fuels to increase their vapor pressure above the liquid. Since the amount of thermal energy is directly related to the quantity of fuel ignited, using the minimum amount of fuel allows safer operation of the apparatus and causes less thermal stress to the equipment and surroundings. In addition to requiring lower fuel flow rates, smaller ignition surfaces are less expensive to purchase than the larger surfaces. Material costs are significant if precious metals or special alloys are included as possible ignition surfaces. Thus the heating, time, fuel, and material considerations all favor keeping the ignition surface as small as possible.

B. SURFACE ORIENTATION

The orientation of the ignition surface relative to the direction of the fuel/air flow can influence the flow patterns on the surface. A 45° approach angle between the surface and the flowing gas stream helps promote good mixing and contact between the surface and the fuel/air mixture. This orientation represents a compromise between parallel and perpendicular geometries. If the surface and flow were oriented parallel to each other (i.e., both vertical or both horizontal), significant boundary layers would develop and impede the mixing process on the heated surface. For fuel/air flow rates of approximately 1 liter/min and a foil width of about 2 cm, the laminar boundary layer thickness would exceed 0.7 cm [7]. If the surface and the fuel/air flow were perpendicular, a stagnation point would develop on the

flow centerline. As the fuel/air mixture remained at or near the stagnation point for extended periods of time, extensive fuel pyrolysis could occur. Such an orientation would create long and ill-defined residence times for the fuel/air mixture near the heated surface - essentially the same problems that currently exist in the conventional ASTM procedure.

C. HEATING THE IGNITION SURFACE

Heating a small surface to 1200 °C can be accomplished directly by electrical resistance or indirectly by using an external heat source. Direct heating allows uniform localized heating if the ignition surface is a conductor and if sufficient electrical energy is available. The temperature can be adjusted by controlling the current flow through the ignition surface. Either AC or DC current can be used to heat the ignition surface. While AC current is efficient, DC current allows more precise control of the surface temperature. The energy necessary to heat a metal surface by allowing electrical current to flow through the metal is proportional to the electrical resistivity and the cross-sectional area available for current flow. Since the electrical resistivity of nickel is about 9 $\mu\Omega$ -cm, preliminary estimates for heating a 10.16 x 2.54 x 0.31 cm strip of nickel suggested that 140,000 Watts would be necessary to reach a surface temperature of 1500 °C. Since the wiring and control elements necessary to handle 140,000 Watts are not trivial, using thinner metal strips is more practical. For the same 10.16 x 2.54 cm strip, a 2.5 μ m thick nickel foil theoretically requires only 800 Watts. Heating thin metal foils via DC current appeared to be the most practical method of heating the ignition surface.

Indirect heating methods were also considered. However, indirect heating of a surface to 1200 °C requires the heater to operate at much higher temperatures. Silicon carbide, molybdenum disilicide, and tantalum heaters all operate at temperatures exceeding 1600 °C. Unfortunately, it is difficult to fabricate silicon carbide and molybdenum disilicide heaters in the smaller sizes (areas less than 4 cm²), and some heater elements droop and sag when hot. Tantalum heaters become brittle when exposed to atmospheric oxygen and would thus require frequent replacement. In addition, the energy from an indirect heater would have to be conducted or radiated to the ignition surface in a uniform manner. The heat source would need to be shielded to preclude it as an ignition source. These problems are sufficiently formidable that direct heating methods were chosen in favor of indirect approaches.

D. FUEL DELIVERY ASSEMBLY

A fuel/air mixture can be directed onto the heated ignition surface via a closed or open delivery system with either a batch or continuous flow process. In a closed system the heated surface would be positioned within an enclosure, and the fuel/air mixture would flow into the enclosure. After the proper fuel-to-air ratio was achieved, the temperature of the surface would be increased until ignition of the fuel charge occurred. The ignition would initiate an explosion within the enclosure, which would have to be constructed to withstand or to vent the explosion. Explosion-proof enclosures would probably prevent viewing the ignition and would reduce access to the ignition

surface. This design would largely prevent the possible use of diagnostic techniques involving gas chromatography, mass spectrometry, and lasers. Explosion venting enclosures would require time consuming and expensive replacement of the blowout panel after each ignition.

Many of the limitations of explosion proof/venting enclosures could be overcome by utilizing an open delivery system, such as a burner, which would allow the fuel/air mixture to ignite in the open at ambient conditions. Since the ignition of the fuel/air charge occurs in an open space, it is not confined and an explosion is avoided. Unencumbered by an enclosure, an open fuel/air delivery scheme also allows easy access for other diagnostic techniques. In addition, the open burner can be matched to the size of the ignition surface more easily than a bulky explosion enclosure. The only significant drawback of an open system is the inability to investigate autoignition phenomena as a function of pressure.

While the closed system would appear to lend itself to batch processing of individual fuel/air charges, the open burner can be operated with either an intermittent batch or continuous flow process. For the closed system a charge or batch of fuel/air mixture would be loaded into the enclosure and the ignition surface would be heated until ignition occurs. As the temperature of the ignition surface was ramped up, the fuel would begin to decompose, resulting in the measurement of an ignition temperature for the pyrolysis products mixed with remnants of the original fuel. This same lack of definition concerning what species are actually igniting plagues the current ASTM procedure. Of course, if the ramp-up times were short, less decomposition would occur, but the steeper the ramping slope, the more difficult it would be to determine the temperature at ignition. The temperature measuring instrumentation would need to have a very short response time.

Batch processing with an open burner would also require an iterative approach but for a different reason. Once the batch or fuel/air charge would begin to flow from the burner, there would be a limited amount of time available to ramp up the temperature before the fuel/air charge would be exhausted. If the initial surface temperature selected were too low and ignition didn't occur before the batch ran out, another batch would be started at a higher initial temperature. Unfortunately, many iterations (or batches) would be necessary to bracket the appropriate temperature range and then pinpoint a precise ignition temperature. The ignition temperature measuring technique would need to have a fast response in order to monitor the ignition temperature before the batch burned itself out. Ignition criteria, such as a sudden rise in surface temperature, might be difficult to establish with certainty if the ignition event did not release much heat relative to the thermal inertia of the surface.

In addition to minimizing fuel decomposition and reducing the number of necessary iterations, a continuous-flow open burner allows one to define unambiguous and easily determined ignition criteria. With a continuous flow of the fuel/air mixture, the surface temperature can be gradually increased until ignition occurs. At this point the fuel/air flow can be shut down and the surface temperature can be reduced. If the flow is turned on again and

allowed to equilibrate, a repeat ignition measurement can be made. The fuel/air flow being directed onto the heated surface is always fresh, and the temperature can be continuously and slowly increased until ignition occurs. Upon ignition, the observation of a flame which is sustained by the continued fuel/air flow clearly marks the ignition point. All of these considerations strongly favor an open system with continuous flow.

Batch processing eliminates the possibility of the ignition flashing back to the fuel supply. For a continuous flow arrangement, a flashback arrestor is required and is straightforward to incorporate into the system.

E. TEMPERATURE MEASUREMENT

Determination of the ignition temperature for each fuel/air mixture requires that the surface temperature be monitored and recorded during each ignition. The instrumentation should not interfere with or alter the ignition process. Additionally, the measurement technique must cover the temperature range of 500 to 1300 °C. Optical pyrometers, film thermocouples, and bead thermocouples all cover this temperature range; however, the last two methods require precautions so as to not disturb the flow or the surface.

An optical pyrometer focussed on the heated surface does not intrude upon the ignition process, but changing surface conditions, such as oxide formation on hot metal surfaces, could affect the surface temperature measurements by changing the surface emissivity. Optical pyrometers measure an average temperature for the circular area or spot where the pyrometer is focussed. An average surface temperature might be desirable if the spot matched the fuel-surface contact area, but if the spot is too large the reported average temperature would be lower than the ignition temperature. The area and location of the spot and the ignition zone would need to be carefully matched for each ignition surface. Certain types of optical pyrometers, such as the disappearing filament design (The Pyrometer Instrument Co., Bergenfield, NJ¹), are too slow and too cumbersome for routine measurement of a changing surface temperature. Optical pyrometers can be periodically used to check thermocouple measurements.

Film thermocouples have been developed to monitor internal cylinder wall temperatures in internal combustion engines [8-10]. These thermocouples are designed to have the same coefficient of thermal expansion as the surface to be monitored. Otherwise, the thermocouple would separate from the hot surface as the local temperature changes. In the present investigation the development of different formulations for each new ignition surface would be expensive and time consuming. Even if the appropriate formulations were available, the film thermocouple could not be bonded to the ignition surface since the thermocouple itself would likely affect the ignition process.

¹ Certain commercial equipment is identified herein in order to adequately specify the experimental procedure. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that this equipment is the best available for the purpose.

Mounting the thermocouple on the back side of the ignition surface prevents interference with the ignition event and with the flow conditions. In this case the thermocouple is not measuring the ignition surface temperature directly but is monitoring a temperature closely proportional to the surface temperature. If the ignition surface were thermally thin, the measured-temperature and heated surface temperature would be essentially the same provided that the thermocouple does not cool the surface.

Bead thermocouples have positioning requirements similar to thin film thermocouples; they are inexpensive and can be quickly replaced when necessary. Minimizing the bead mass provides a fast response time. Sheathing the thermocouple in a durable material such as stainless steel increases the useful lifetime of each thermocouple without sacrificing performance. Routine temperature measurements with an optical pyrometer provide a means to relate the thermocouple temperature values to the actual surface temperatures. Sheathed, beaded thermocouples were used in the present investigation to monitor surface temperatures.

SECTION III
TEST METHOD FOR MEASURING SHORT DURATION AUTOIGNITION TEMPERATURES:
DESIGN AND OPERATION OF THE APPARATUS

A new apparatus has been designed, built, and extensively tested for making short-duration autoignition temperature measurements of hydrocarbon fuels under conditions where the fuel/air stoichiometry, the nature of the hot metal surface, and the contact time are well controlled. The following paragraphs present the details of our experimental procedures.

A. APPARATUS

The apparatus includes two direct current (DC) power supplies, a foil holder, fuel and air flow controllers, a premixed flame burner assembly, bubblers to vaporize liquid fuels, and a data acquisition computer. A schematic layout is presented in Fig. 1. There are two key elements: the premixed flame burner assembly and the holder for thin metal foils.

1. Burner

The burner assembly consists of a Perkin-Elmer body and a custom burner head of 1.1 cm diameter made from 61 capillary tubes to prevent flashback upon ignition. This allows a known and easily variable mixture of hydrocarbon fuel and air to be directed toward the hot metal surface (see Fig. 1). Flow controllers allow different mixtures of air and fuel to be introduced. Mixing fins within the burner body ensure thorough mixing of the fuel and air. A 2.2 cm long by 1.1 cm diameter quartz chimney isolates the fuel-air mixture from ambient air until the flow is within 0.64 cm of the hot surface. The lighter hydrocarbons are drawn from high-pressure gas cylinders and are mixed with dry filtered low-pressure air to achieve the desired stoichiometry. For the heavier hydrocarbons which have lower vapor pressures, the liquid hydrocarbon is placed in glass bubblers located in a 30 °C water bath (only 5 degrees above ambient conditions). The temperature and pressure of the bubblers determine how much hydrocarbon vapor will be picked up by the air passing through the bubblers. In our experiments the temperature of the bubblers was fixed at 30 °C, and the air flow through the bubblers was adjusted to obtain the desired stoichiometry. The air passes through a series of three bubblers to ensure saturation of the air stream. This air stream is then mixed with dry filtered air in the burner assembly to obtain the proper stoichiometry. Once ignition occurs, the appearance of the burner-stabilized flame establishes a reproducible and reliable ignition criterion. The onset of ignition is detected both visually and by thermocouple readings.

2. Fuel Flow Rate

Operating at low flow rates is desirable, since the fuel vapor pressure decreases as the fuels increase in molecular weight - making it more difficult to vaporize sufficient quantities of liquid fuels to sustain ignition. Since the flow rate of the fuel/air mixture affects the contact

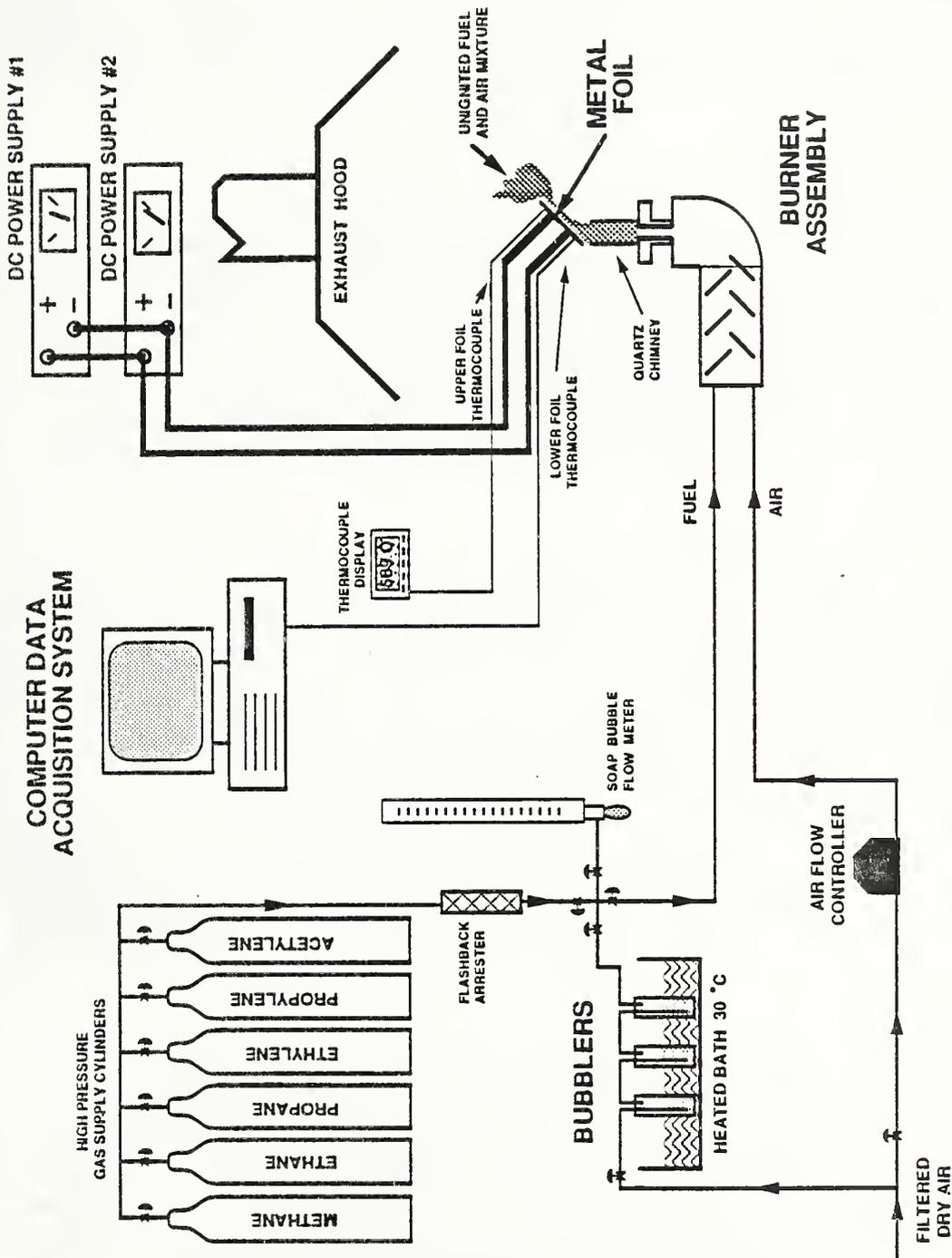


Figure 1. Schematic Diagram of the Apparatus for Making Short-Duration Autoignition Temperature Measurements.

time and mixing at the heated surface, a series of autoignition temperature measurements was conducted at 8, 12, 16, 24, and 32 cm/s in order to select an appropriate fuel/air velocity exiting the burner. Figure 2 shows that the observed autoignition temperatures for ethylene/air mixtures igniting on a nickel surface are relatively independent of the velocity. There is some indication that the autoignition temperature decreases at the highest velocity of 32 cm/s. A fuel/air velocity of 16 cm/s was selected for making all of the remaining autoignition temperature measurements. With this flow velocity exiting the quartz chimney located above the burner, the volumetric flow rate was approximately 912 cm³/min.

3. Contact Time on the Foil Surface

The fuel/air mixture flows near the heated surface for an estimated 90 milliseconds. This value is obtained from the approach velocity (16 cm/s), the surface orientation (45°), and the heated surface length (2.06 cm). Possible mixing effects were not included in the calculated contact time, and effects due buoyancy induced by heating of the gas as it passes near the surface were not considered. This duration of less than 0.1 seconds is significantly shorter than the several minute residence times reported by other researchers for making autoignition temperature measurements using the ASTM apparatus [11-15]. The short residence times of the present investigation greatly reduce the extent of fuel decomposition.

4. Holder for the Heated Metal Surface

The second key element of our apparatus is the holder for the thin metal foils, which also includes local temperature measurement capability (shown in Fig. 3). The temperature of the metal foil increases as the DC current flows through the foil (typical dimensions are 2.54 x 10.16 x 0.013 cm). About 40 amps are necessary to heat nickel foil up to 1000 °C. Although notching each foil at the lower edge on the centerline forces the center of the foil to heat up more than the ends, the foil ends still become sufficiently hot that expansion can cause loss of electrical contact. This is prevented by spring loading the electrodes to maintain electrical contact as the foil expands. Since the foil also expands lengthwise, the holder applies tension to stretch the foil. This stretching preserves the 45° approach angle of the fuel/air mixture, helps to prevent gas flow behind the foil, and maintains good contact with the two chromel-alumel thermocouples positioned behind the foil.

5. Metal Surfaces

The four materials selected for surfaces in this study included nickel (99.9% Ni), stainless steel (304 series), titanium (99.9%), and aluminum. These metals were purchased as 2.54 x 10.16 cm foil strips. The appropriate thickness of each foil was determined by the metal's electrical resistivity and by the cost of rolling it into a foil. The electrical resistivities of 3, 9, 70, and 160 μΩ-cm and rolling costs of 3, 13, 10, and 16 dollars (per piece) suggested thicknesses of 10, 12.7, 5.1, and 25.4 μm for aluminum, nickel, stainless steel, and titanium, respectively. Attempts to use aluminum as an ignition surface failed because of its relatively low melting point. As the aluminum foil was heated to temperatures of approximately

Autoignition Temperatures vs Fuel /Air Velocity

Ethylene / Air, $\phi = 1.0$, on Nickel Foil

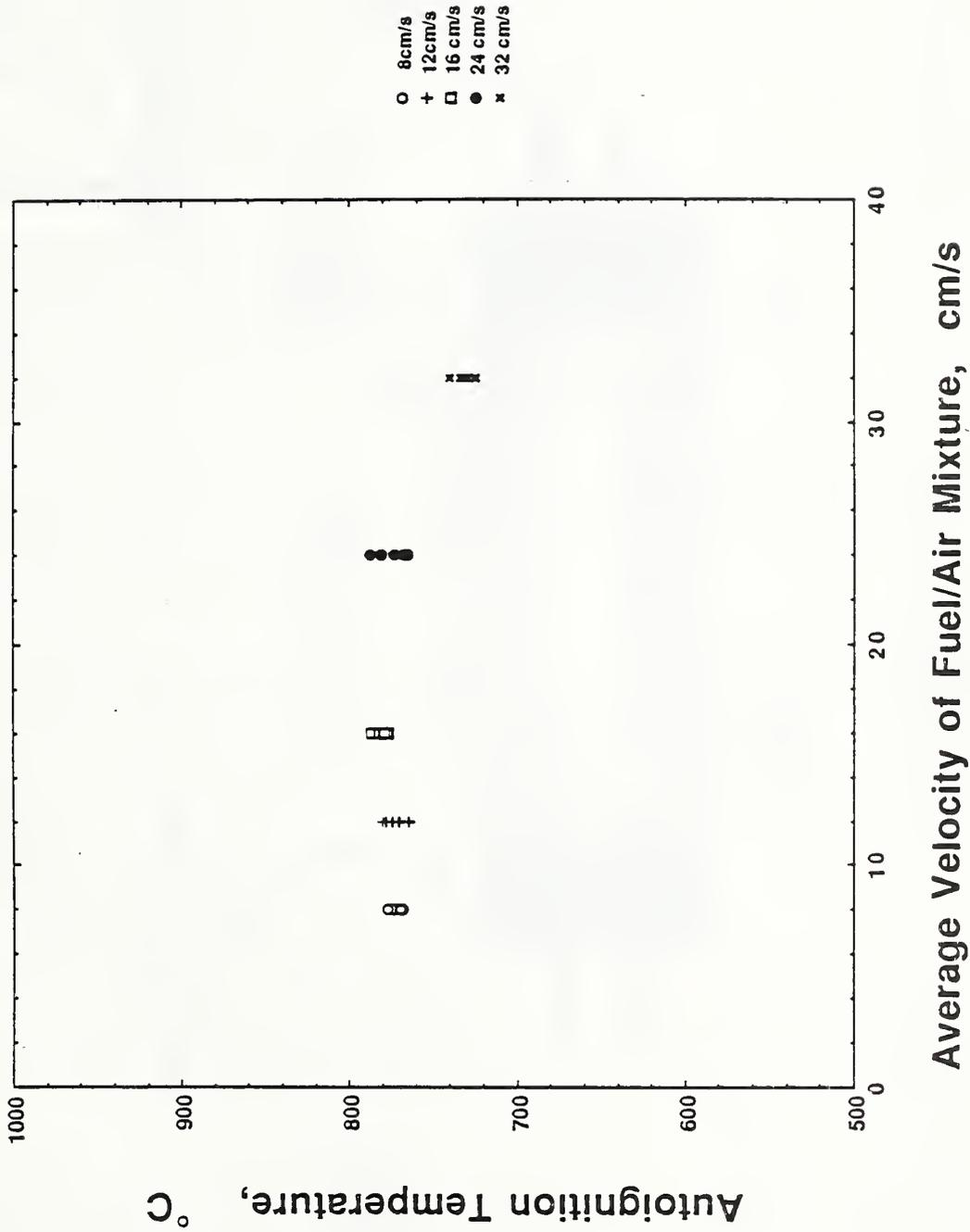


Figure 2. Measured Autoignition Temperatures as a Function of Flow Velocity for Ethylene/Air Mixtures ($\phi = 1.0$) on a Heated Nickel Surface.

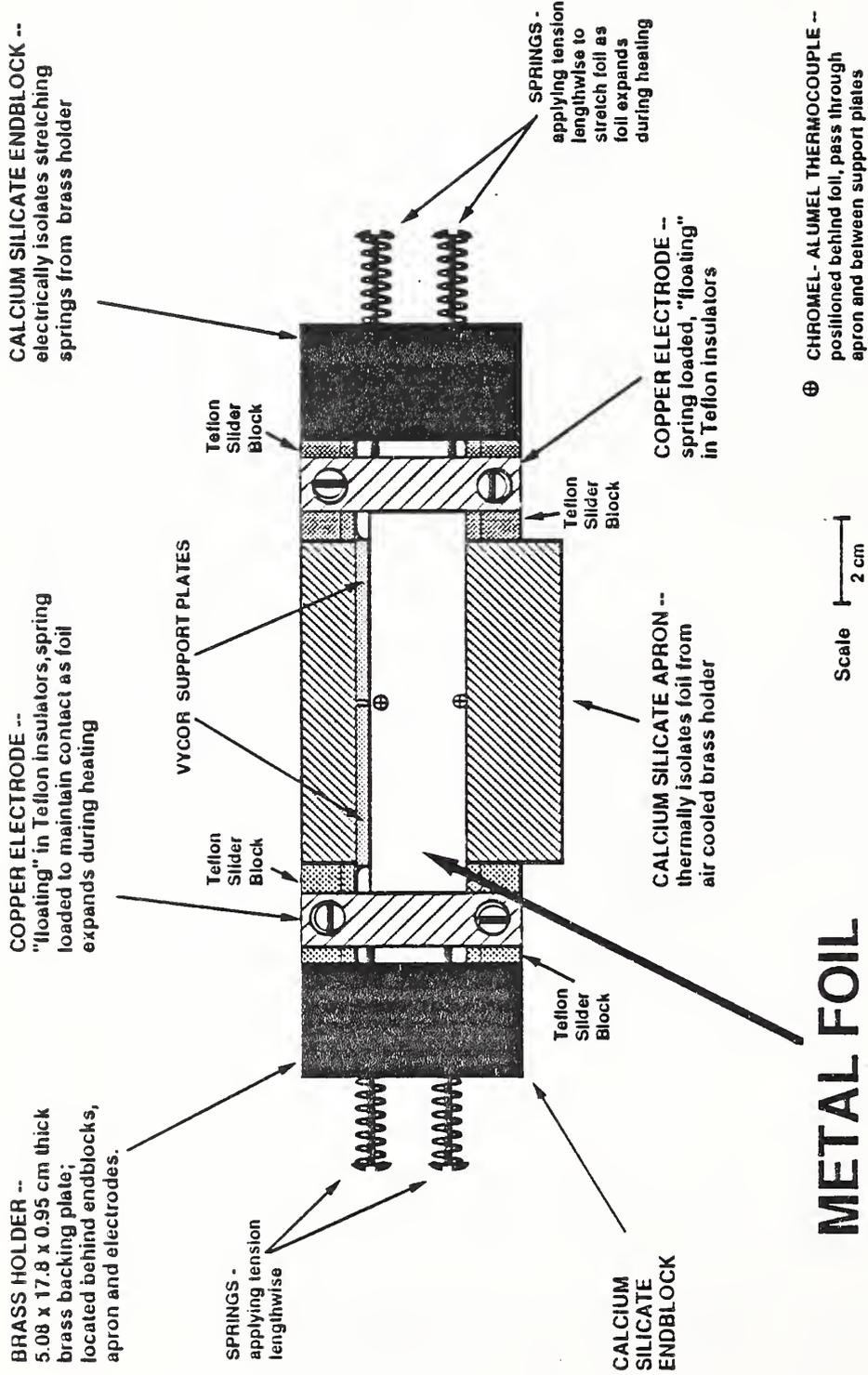


Figure 3. Schematic Diagram of the Holder for Thin Metal Foils.

500 °C, the foil began to melt and lost its tensile strength. The tension which was necessary to hold the foil against the thermocouples separated the softened foil into two pieces.

An unsuccessful attempt was made in the present study to extend some earlier experimental work by Pfefferle et al. [5,6] which utilized extremely thin ($\approx 1 \mu\text{m}$) films of platinum on a quartz substrate. Thin films of nickel metal were vacuum deposited onto 0.16 and 0.32 cm thick Vycor substrates. One surface of each 2.54 x 7.62 cm substrate was coated with a $1 \mu\text{m}$ thick layer of nickel. The nickel layer thickness was doubled to $2 \mu\text{m}$ on both ends of the substrate to improve the electrical contact necessary for resistance heating. After clamping each film/substrate into a holder, DC current was applied to heat the center section of the thin film. As the film reached a temperature of approximately 300 °C, the film began to break down and lost electrical continuity.

This structural failure of the $1 \mu\text{m}$ thin films was surprising, since such difficulties were not reported in the original papers [5,6]. However, upon consultation with Professor Pfefferle and her students, it was discovered that their film deposition technique required multiple layers, with each layer being annealed individually. The specific time and temperature for each annealing cycle were empirically determined over a period of many months. Even after carefully following the multi-layering/annealing process, reproducible performance of the surface was not guaranteed. Since it appeared that much time would be required to develop such annealing procedures for our experiments on different metal surfaces, the effort to use thin film resistance heaters was discontinued in favor of the metal foils.

6. Thermocouple Measurements

Fast response sub-miniature stainless steel sheathed chromel-alumel thermocouple probes were used to monitor the foil temperatures (Omega, Stamford, CT). Each foil was supported from behind by two thermocouples. The upper thermocouple was positioned 0.16 cm down from the upper edge of the foil, while the lower thermocouple was located 0.32 cm up from the lower edge (see Fig. 3). The recommended operating range for chromel-alumel bead thermocouples is -200 to 1260 °C. The thermocouple probes utilized $38 \mu\text{m}$ wires within a 0.25 mm diameter 304 stainless steel sheath. An estimated 0.4 second would be required for the thermocouple to reach 63.2% of the instantaneous temperature change [16]. Each thermocouple bead was electrically insulated from the sheath with magnesium oxide. These insulated or ungrounded thermocouples were necessary to isolate the temperature voltage (millivolts) from the heating voltage (up to 20 volts). As each thermocouple probe was exposed to the hot surfaces, the $38 \mu\text{m}$ wires became brittle. Eventually thermal or mechanical stress caused the embrittled wires to break, necessitating the replacement of the thermocouple probe.

7. Liquid Fuel Vaporization

Liquid fuels were vaporized by saturating a portion of the air stream by bubbling the air through gas washing bottles filled with the fuel. The appropriate amount of fuel to be added to obtain overall stoichiometries of

0.7, 1.0, and 1.3 was determined from published values of vapor pressure versus temperature for each fuel [17]. Four pairs of the 125 ml glass gas washing bottles or bubblers were arranged in parallel to reduce the air flow rate through any single pair of bubblers. The air/fuel flow from the four pairs of bubblers was finally collected into a single 500 ml bubbler, so that each air stream passed through a total of three bubblers. Reducing the flow rate allowed the air to become more fully saturated as it bubbled through the liquid fuel. Breaking the gas flow up into many small bubbles via fritted glass sparging disks also helped to saturate the air with fuel. Clamps on the tubing connecting the bubblers were used to direct the air flow evenly through all of the bubblers. A pressure tap on the 500 ml collection bubbler allowed the pressure above the liquid fuel to be monitored.

An insulated, well-mixed water bath was used to keep the bubblers at specific temperatures. A 0.2 hp circulation pump constantly mixed the bath while three heaters maintained the desired water temperature, which was monitored using a chromel-alumel thermocouple submerged in the bath. Due to size limitations of the insulated container only the last four parallel bubblers and the collection bubbler were placed in the water bath. The first four parallel bubblers were at room temperature, typically 25 ± 3 °C. Increased temperatures (up to 30 °C) were necessary to raise the vapor pressure of the heavier liquid fuels to obtain the needed flow rates.

8. Data Acquisition System

For data acquisition an IBM XT computer was equipped with a Metrabyte DASCON-1 multifunctional analog/digital expansion board, which features four input/output channels with 12 bit resolution. For each temperature data point the computer recorded five thermocouple voltages, averaged the five values, converted the voltage to a temperature, and reported a single data point at approximately 0.5 second intervals. A cold junction compensator in the thermocouple line eliminated the need for a reference thermocouple. The computer also recorded a second channel which was used to mark each ignition event. When not activated, the marker channel voltage was less than 1 volt. Upon visual observation of ignition, a push-button was depressed and the marker channel voltage was increased to 1.5 volts. The subsequent peak in the marker channel voltage identified each ignition event. At each time step the computer recorded the time, the thermocouple voltage, the foil temperature, the marker channel voltage, and the step number. After each ignition series the computer transferred the data file to the hard disk drive. Software retrieved the data and plotted the time versus temperature and time versus marker channel on the same graph. Figure 4 is an example of the plotted data for a single ignition.

B. OPERATION

1. Foil Preparation

Before mounting on the holder, each foil was notched and folded to induce localized uniform heating, to prevent flow disturbances, to reduce flow behind the foil, and to improve the foil stretching characteristics. A 0.32 cm wide by 1.27 cm semicircular section was removed from the center of

T900628a.dat Benzene / Air, $\phi = 1.0$,
on Nickel Foil

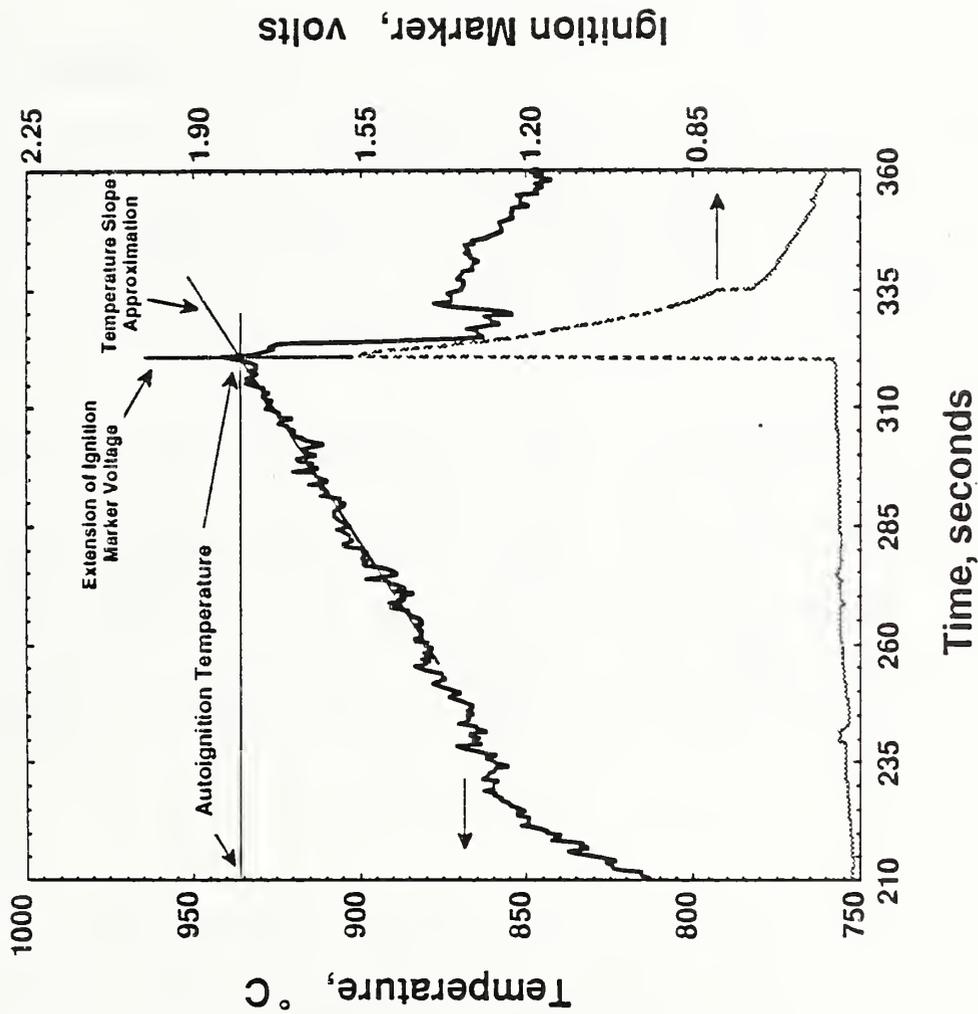


Figure 4. Temperature as a Function of Time for a Benzene/Air Mixture ($\phi = 1.0$). Also shown is the voltage record of the ignition marker. The intersection of the two lines indicates the autoignition temperature (see text, Section III.B.5).

the lower edge of each foil. This notch reduced the cross-sectional area for current flow and forced heating to occur preferentially at the center of the foil. Without this notch, foil imperfections or strain associated with stretching caused non-uniform and unpredictable hot zones. If this notch were exposed to the fuel/air flow over the front surface of the foil, it could introduce disturbances in the flow. To avoid this flow disturbance and to prevent the flow of the fuel/air mixture behind the foil, a 0.48 cm wide strip along the lower edge of the foil was folded over at 90 degrees. As the foil was mounted on the holder, 0.32 cm of this lip slipped into a recessed slot. The partially recessed leading edge of the foil "hides" the notch and prevents fuel/air flow behind the foil.

2. Foil Mounting and Burn-in

After each foil was notched, trimmed, and folded, it was placed on the holder and positioned over the two thermocouples. Before tightening the electrode springs, stainless steel shims were inserted with the foil ends to provide a better grip on the foil. After tightening the electrode springs, the stretching springs were adjusted to stretch the foil over the thermocouples. The DC current was then adjusted to heat the foil in 50-75 °C steps. As the temperature of the foil increased, the foil expanded and began to move away from the supporting thermocouples. As the foil began to lose contact, the current was turned off, the foil was retightened, and the current was quickly turned on again before the foil cooled to ambient temperature.

As each foil was burned in, the current levels and foil temperatures were recorded for diagnostic purposes. Nickel and titanium usually did not require much tightening after the initial mounting. The stainless steel stretched and expanded to a much greater extent and required several iterations of heating to ≤ 600 °C, tightening and then heating, further tightening, etc. Typically the lower thermocouple reported temperatures 50 to 100 °C higher than the upper thermocouple, due to the increased current flow near the notch in the foil. The upper thermocouple was used for diagnostic purposes as a check that the apparatus was operating properly. Recording temperature versus the current flow allowed the operator to detect conditions of loose foil and malfunctioning thermocouples.

3. Flow Measurement, Calibration, and Calculation

Small rotameters and mass flow controllers were used to control the flow rate of the hydrocarbon fuels and the air for combustion and cooling. Before each ignition series a soap bubble flowmeter was used to calibrate the smaller flow rate, usually the fuel flow. Mass flow controllers calibrated periodically using a large soap bubble flowmeter were employed to control the larger flow rate, typically the combustion air flow and the cooling air flow. The mass flow controllers had ranges of 0 to 5 and 0 to 1 liter/min. Two small rotameters with flow capacities of 4 to 100 and 50 to 500 cm³/min were utilized to monitor the smaller flow rates. For the heavier hydrocarbons almost all the combustion air had to be bubbled through the bubblers so the mass controllers monitored the "fuel" flow.

Each hydrocarbon fuel was ignited under stoichiometric fuel/air conditions ($\phi = 1.0$), which provide sufficient oxygen for complete conversion of the fuel to carbon dioxide and water. The fuels were also ignited under lean ($\phi = 0.7$ or 70% of fuel required for stoichiometric conditions) and rich conditions ($\phi = 1.3$). The overall burner flow rate was multiplied by the specific volume fraction to obtain the volumetric flow rate of the fuel necessary for the desired stoichiometry. For each of the gaseous fuels the flow rate was calibrated and set using a soap bubble flowmeter. During the ignition series the fuel flow rate was recorded but not adjusted. The fuel flow rates were typically very steady and did not drift significantly over the 10 to 15 minutes required for an ignition series. After the fuel flow rate was established, sufficient combustion air was added to provide a total flow rate of 912 cm³/min. Calibrating the fuel flow rates for the liquid hydrocarbons followed the same pattern as the gaseous fuels, but included vapor pressure calculations.

The flow rate calculations for the liquid fuels incorporated the specific stoichiometry, ambient pressure, bubbler pressure, bath temperature, and vapor pressure for each hydrocarbon fuel. Before an ignition series an atmospheric pressure reading was obtained from a wall-mounted mercury barometer. The vapor pressure of each hydrocarbon fuel was obtained from plots of vapor pressure versus temperature [17]. Using the atmospheric pressure, the fuel vapor pressure at the temperature of the water bath, and the desired stoichiometry, the flow rate through the bubblers was estimated and the flow was adjusted to this value. With the flow rate near the final expected value, the bubbler pressure was recorded and included with the vapor and ambient pressures in a second fuel flow rate calculation.

The calculations outlined above are based on the assumption that the air passing through the bubblers was completely saturated. Thus, the fraction of the liquid fuel in the bubbler flow was taken to be equal to the vapor pressure of the fuel divided by the sum of the atmospheric and bubbler pressures. Dividing the volumetric flow rate of pure fuel for a specified stoichiometry by this fraction of the fuel in the bubbler flow described the flow rate of air which must be supplied to the bubblers to provide the required amount of fuel at the burner. Subtracting the bubbler flow rate from the total flow rate yielded the flow rate for the combustion air necessary for the specified stoichiometric conditions. The bubbler flow rates were calibrated before each ignition series using the soap bubble flowmeter.

4. Ethylene Benchmark Autoignition Temperature Measurements

After each foil was mounted and burned in, a typical ignition series using an ethylene/air mixture was conducted to help characterize foil performance. This benchmark ethylene series also provided comparison of foil performance between different foils of the same material. The ethylene ignitions allowed fine tuning of the foil, the sample holder, and the thermocouple performance before actually making autoignition temperature measurements for specific hydrocarbon fuels.

5. Autoignition Temperature Measurements

After making the ethylene benchmark temperature measurements, each specific hydrocarbon fuel/air mixture was introduced onto the heated metal surface. The surface temperature was increased at a rate of approximately 60 °C/min until ignition occurred. This first or zeroth ignition was monitored but not recorded for future data analysis. The zeroth ignition helped to define a temperature range where subsequent ignitions were probable and helped to establish a reasonable initial foil temperature 50 to 75 °C below the ignition temperature. After adjusting the foil to this initial temperature, the data acquisition system was reset and a series of 5 ignitions was initiated. Typically the fuel/air mixture was allowed to flow and equilibrate for 45 seconds. After this equilibration time the ignition surface temperature was increased by approximately 30 °C/min until ignition occurred.

After ignition the fuel flow and occasionally the air flow were shut down to allow the flame to burn itself out. This normally required less than 15 seconds. The fuel and air flow were then restarted and allowed to flow and equilibrate for 45 seconds before again ramping up the surface temperature. Five repeat temperature measurements required from 8 to 19 minutes to complete; a typical ignition series lasted about 12 minutes.

Surface temperatures were also checked with an optical pyrometer. When the disappearing filament was positioned close to the lower thermocouple, the pyrometer temperatures were found to be 50-60 °C higher than the thermocouple values for typical operating conditions ($T = 700-1000$ °C). Some local cooling of the heated foil was evident by the appearance of dark spots at the positions of the thermocouples. All temperature values reported in the next section are the thermocouple determinations.

After each ignition series the computer transferred the data file to the hard disk drive, and software plotted the temperature versus time and the marker channel versus time on the same graph. On each plot for each ignition event a vertical line was extended from the 1.5 volt peak on the marker channel, shown on Fig. 4. A second straight line, which approximated the slope of the temperature versus time curve just before ignition, was also drawn on each plot. The intersection of these two lines was recorded as the autoignition temperature.

SECTION IV RESULTS

Over 1100 individual autoignition temperature determinations have been made in the present study. Table 1 summarizes these data for the ignition of 15 hydrocarbon fuels on heated nickel, stainless steel, and titanium surfaces for three stoichiometries. The entries are averaged autoignition temperature values with a stated error of one standard deviation for usually at least five repeat determinations.

All the benchmark runs are included in Table 1 for the reported ethylene values at $\phi = 1.0$. The number of benchmark ignitions is 90, 67 and 112 for nickel, stainless steel, and titanium, respectively. The reproducibility of these measurements within a single ignition series on a given day is excellent, often within 1% and never exceeding a variation of 3.2%. The reproducibility of igniting a specific hydrocarbon fuel on different pieces of the same foil material with different thermocouples at different times (sometimes separated by months) is somewhat worse than the reproducibility within a single series. Maximum month to month (foil to foil) variations in autoignition temperatures between repeat ignition series for a specific fuel are 6.9, 9.0, and 7.7% for nickel, stainless steel, and titanium surfaces, respectively. Figure 5 illustrates this measurement reproducibility for a series of five benzene ignitions on a nickel surface. For each curve the ignition temperature is indicated (see Section III.A.8); all five values lie within a narrow 10 °C temperature range.

Figures 6a and 6b present both individual and averaged data for ethylene ignitions on a nickel surface over an extended range of stoichiometries. These results also show the good reproducibility of the measurements for repeat determinations. In addition, the data reveal that the autoignition temperature decreases slowly for the richer fuel/air mixtures. This trend was observed for most of the hydrocarbon fuels investigated on the three metal surfaces (see Table 1). In about 45% of the fuel/surface/stoichiometry cases the autoignition temperatures exhibited a minimum at $\phi = 1.0$. In only one case (propane on nickel) does the autoignition temperature exhibit a distinct maximum at $\phi = 1.0$.

Additional measurements were also made for acetylene over a wide range of stoichiometries for two reasons: (1) this fuel exhibits exceptionally wide flammability limits [18], and (2) acetylene autoignition temperatures are observed to be the lowest of any fuel in this study. The results are summarized in Table 2. Again, the autoignition temperature is observed to decrease with increasing fuel/air ratio, particularly for the richest conditions.

The variation of the measured autoignition temperatures with the heated metal surface is presented in Figs. 7a (nickel), 7b (stainless steel), and 7c (titanium). All the data are shown for stoichiometric ($\phi = 1.0$) ignition conditions. The highest temperatures are observed for the nickel surface, while the lowest data points are for the stainless steel surface - often by as much as 200 °C. The titanium data are intermediate.

Table 1. Measured Autoignition Temperatures ($^{\circ}\text{C}$).

ϕ	<u>Nickel Foil</u>			<u>Stainless Steel Foil</u>			<u>Titanium Foil</u>		
	0.7	1.0	1.3	0.7	1.0	1.3	0.7	1.0	1.3
Methane	1094 \pm 6	1040 \pm 10	974 \pm 22	979 \pm 4	814 \pm 8	941	1059	1038 \pm 8	976 \pm 10
Ethane	898 \pm 6	896 \pm 18	885 \pm 33	776 \pm 5	767 \pm 3	768 \pm 7	831 \pm 14	810 \pm 34	794 \pm 14
Ethylene	860 \pm 6	803 \pm 24	852 \pm 6	762 \pm 5	715 \pm 20	752 \pm 2	781 \pm 10	768 \pm 24	729 \pm 8
Acetylene	758 \pm 5	711 \pm 5		672 \pm 10	662 \pm 3		671 \pm 9	655 \pm 4	
Propane	914 \pm 4	982 \pm 7	893 \pm 7	803 \pm 4	805 \pm 4	805 \pm 4	923 \pm 17	847 \pm 8	790 \pm 15
Propylene	1005 \pm 6	1004 \pm 9	1015 \pm 23	830 \pm 10	813 \pm 6	757 \pm 4	920 \pm 3	909 \pm 10	929 \pm 5
Butane	928 \pm 4	939 \pm 5	955 \pm 2	797 \pm 6	784 \pm 5	775 \pm 5	881 \pm 9	807 \pm 6	821 \pm 5
1-3 Butadiene	969 \pm 2	959 \pm 6	952 \pm 11	766 \pm 5	755 \pm 4	730 \pm 7	850 \pm 10	786 \pm 7	851 \pm 18
n-Pentane	934 \pm 4	941 \pm 6	939 \pm 8	778 \pm 4	722 \pm 7	751 \pm 6	878 \pm 10	808 \pm 4	835 \pm 9
n-Hexane	912 \pm 6	905 \pm 5	916 \pm 5	792 \pm 3	775 \pm 6	773 \pm 4	819 \pm 15	799 \pm 8	796 \pm 10
Benzene	913 \pm 3	937 \pm 4	920 \pm 6	770 \pm 11	743 \pm 6	770 \pm 12	854 \pm 19	868 \pm 1	810 \pm 7
Cyclohexane	997 \pm 9	931 \pm 4	922 \pm 5	811 \pm 9	788 \pm 11	798 \pm 6	860 \pm 8	835 \pm 9	841 \pm 13
n-Heptane	909 \pm 9	897 \pm 6	890 \pm 7	806 \pm 10	789 \pm 9	813 \pm 6	856 \pm 12	850 \pm 11	907 \pm 9
n-Octane	920 \pm 19	893 \pm 10	826 \pm 22	830 \pm 17	826 \pm 8	782 \pm 8	891 \pm 7	877 \pm 11	883 \pm 4
iso-Octane	1141 \pm 23	953 \pm 10	977 \pm 5	850 \pm 10	839 \pm 9	841 \pm 3	946 \pm 8	890 \pm 10	900 \pm 17

Notes: ϕ is the fuel/air ratio, where $\phi = 1.0$ represents stoichiometric conditions for complete combustion to yield CO_2 and H_2O . The quoted errors represent one standard deviation for repeat measurements (typically 5).

T900628a.dat Benzene / Air, $\phi = 1.0$
on Nickel Foil

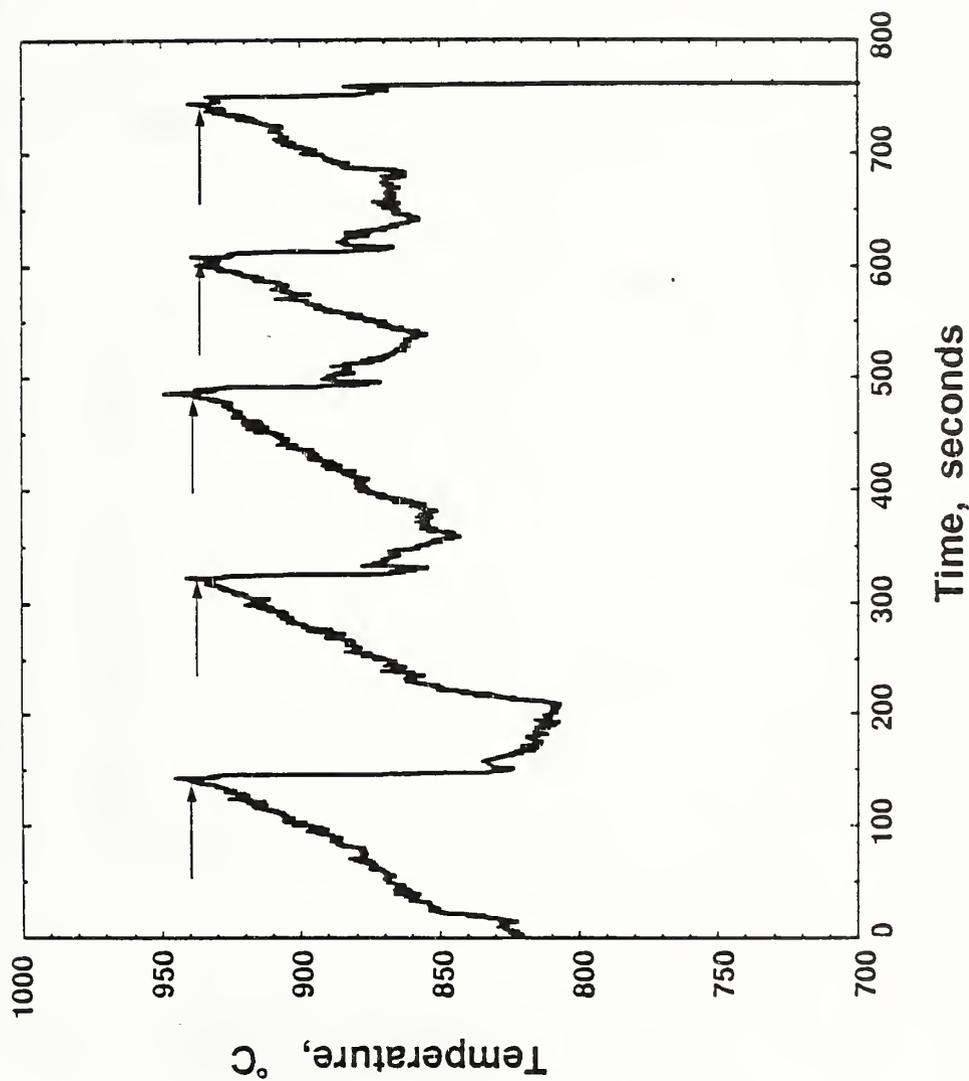
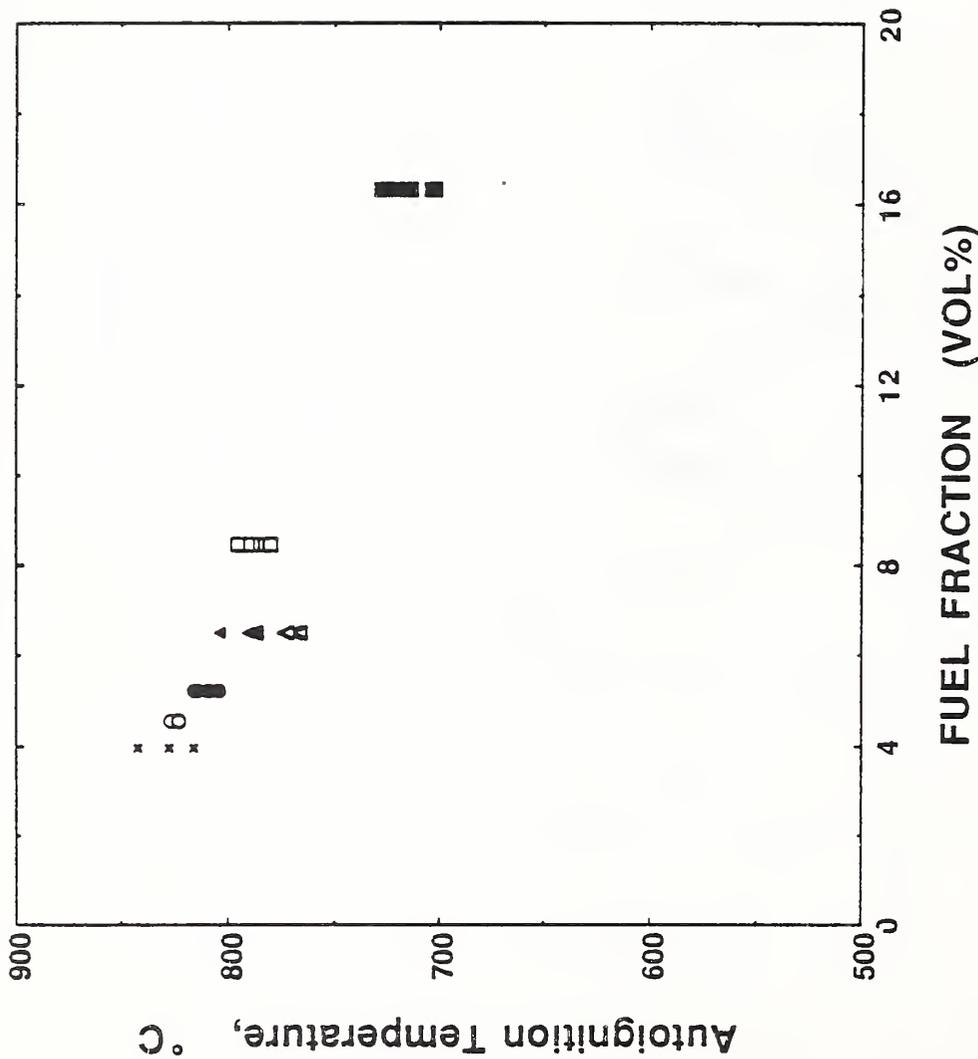


Figure 5. Temperature as a Function of Time for a Benzene/air Mixture ($\phi = 1.0$) for Five Repeat Determinations of the Autoignition Temperature. The individual values of the autoignition temperatures are indicated by arrows.

**AUTOIGNITION TEMPERATURE VS FUEL FRACTION
ETHYLENE on NICKEL FOIL**



- △ 6.5% C₂H₄, $\phi = 1.0$
- × 3.96% C₂H₄, $\phi = 0.6$
- 4.56% C₂H₄, $\phi = 0.7$
- 5.23% C₂H₄, $\phi = 0.8$
- ▲ 6.5% C₂H₄, $\phi = 1.0$
- 8.47% C₂H₄, $\phi = 1.3$
- 16.32% C₂H₄, $\phi = 2.5$

Figure 6a. Measured autoignition temperatures as a function of fuel/air stoichiometry for an ethylene/air mixture ($\phi = 1.0$). Multiple measurements are shown to illustrate reproducibility.

**AVERAGE AUTOIGNITION TEMPERATURE VS FUEL FRACTION
ETHYLENE on NICKEL FOIL**

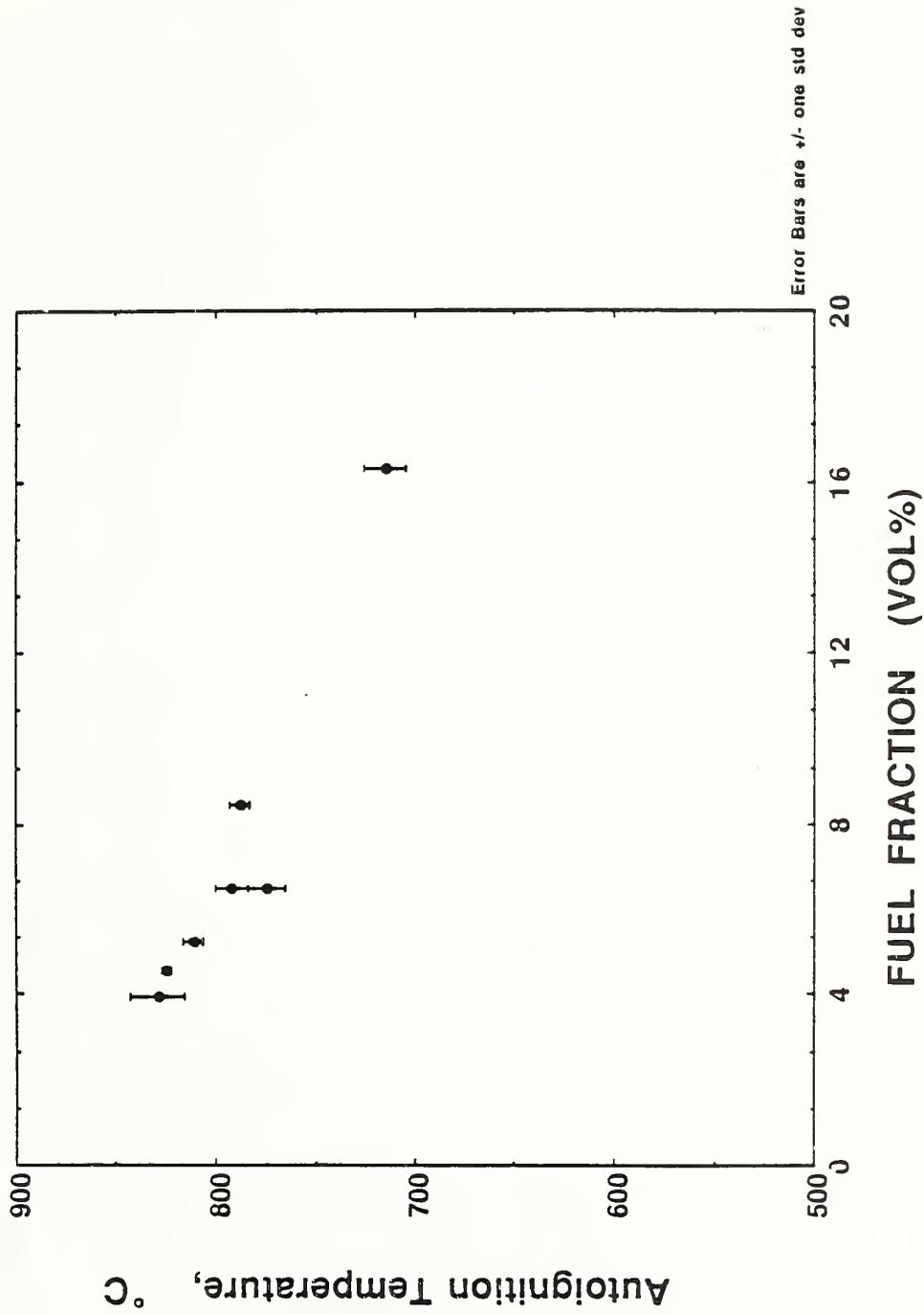


Figure 6b. Average Autoignition Temperatures as a Function of Fuel/Air Stoichiometry for an Ethylene/Air Mixture ($\phi = 1.0$).

Autoignition Temperature vs Carbon Number
Nickel Surface - All Hydrocarbon Fuels

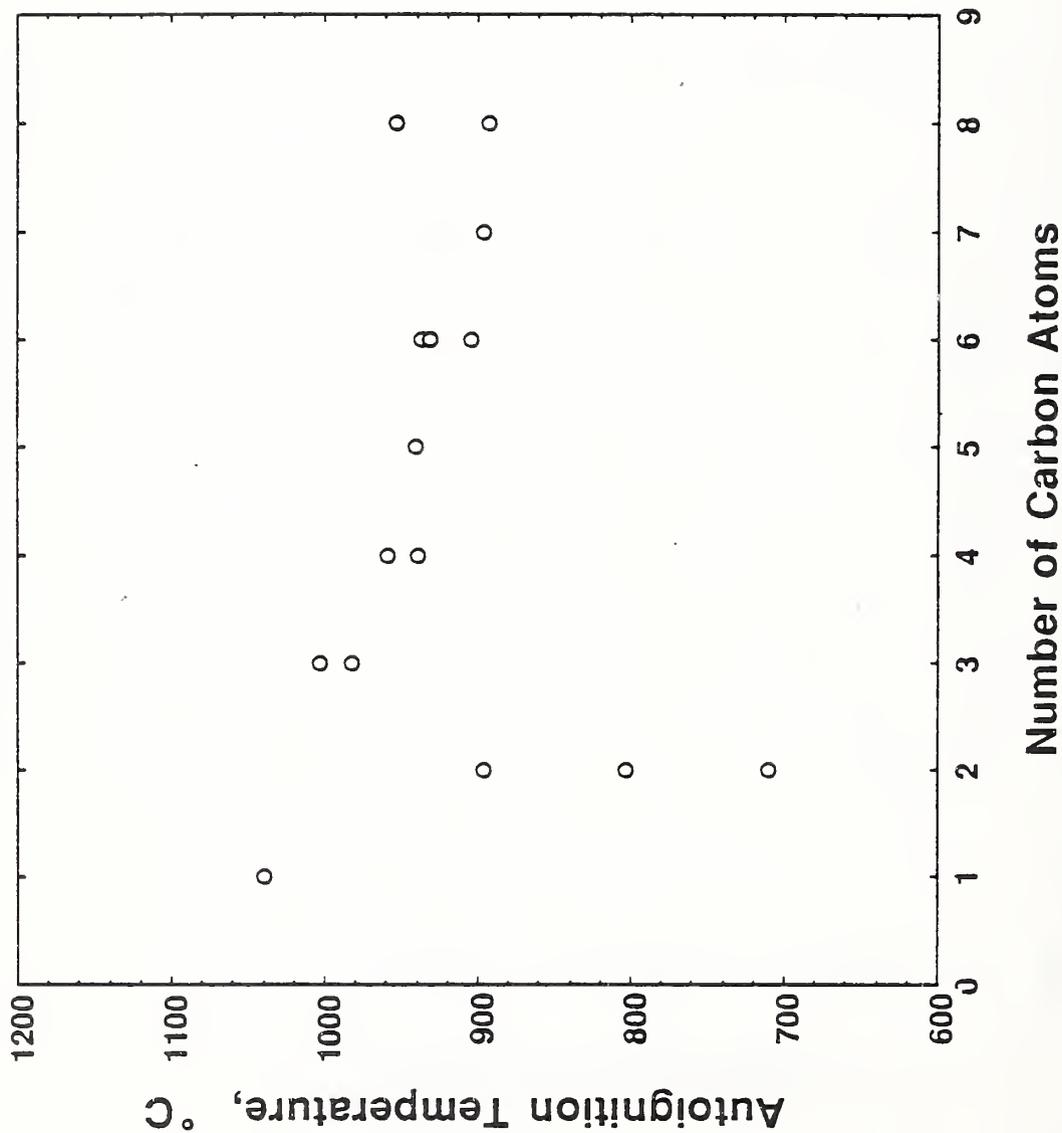


Figure 7a. Measured Autoignition Temperature as a Function of Carbon Number for All of the Fuels Investigated ($\phi = 1.0$) on Nickel Surface.

Autoignition Temperature vs Carbon Number
Stainless Steel Surface - All Hydrocarbon Fuels

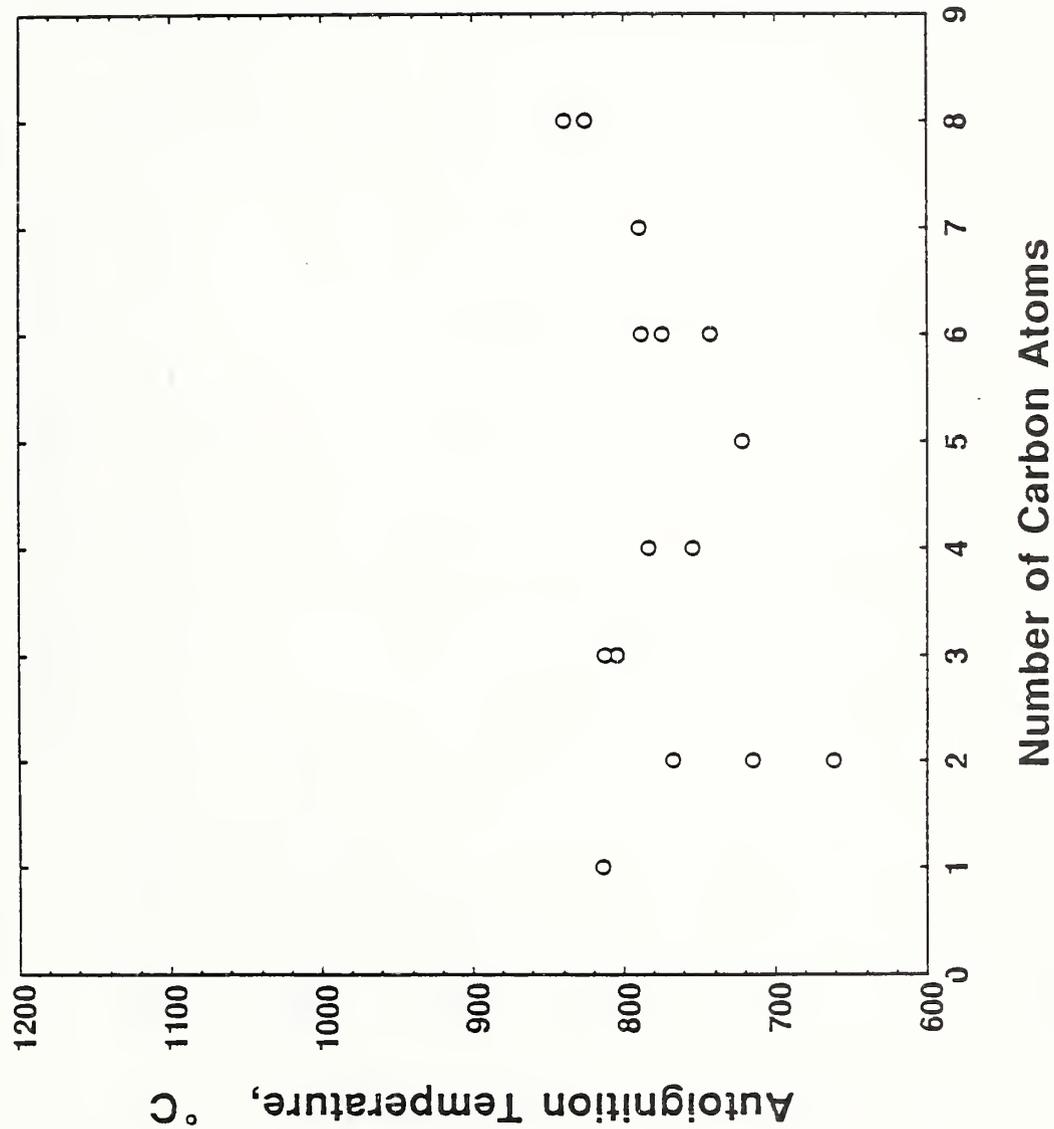


Figure 7b. Measured Autoignition Temperature as a Function of Carbon Number for All of the Fuels Investigated ($\phi = 1.0$) on Stainless Steel Surface.

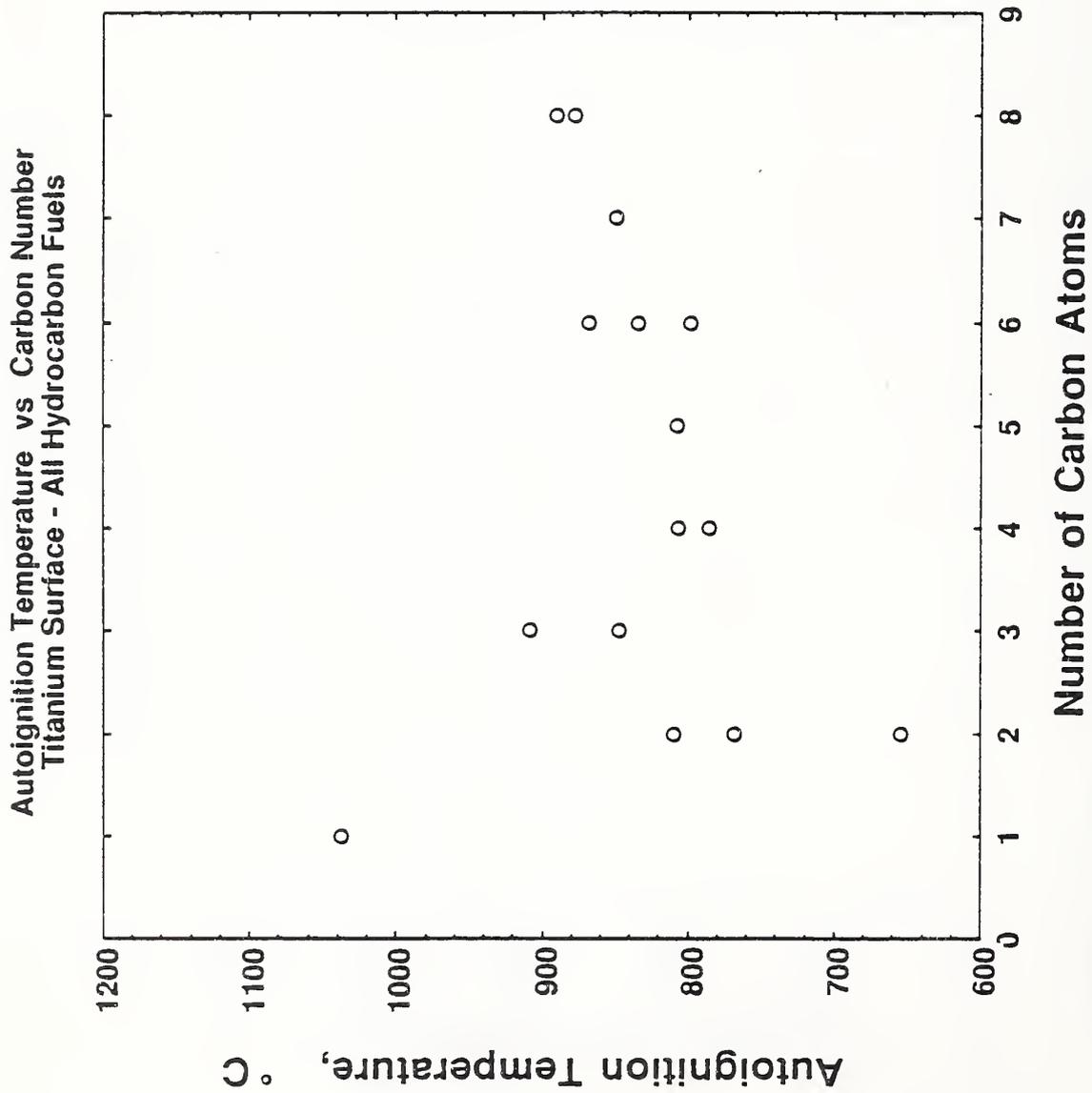


Figure 7c. Measured Autoignition Temperature as a Function of Carbon Number for All of the Fuels Investigated ($\phi = 1.0$) on Titanium Surface.

Table 2. Autoignition Temperatures for Acetylene (°C).

ϕ	Nickel Foil	Stainless Steel Foil	Titanium Foil
0.35	763 \pm 2	687 \pm 3	731 \pm 5
0.50	756 \pm 2	678 \pm 8	732 \pm 9
0.70	758 \pm 5	672 \pm 10	671 \pm 9
1.0	711 \pm 5	662 \pm 3	656 \pm 4
2.0	651 \pm 10	588 \pm 7	659 \pm 2
3.0	627 \pm 9	530 \pm 4	593 \pm 12
4.0	557 \pm 5	492 \pm 9	556 \pm 17

SECTION V COMPARISON WITH LITERATURE VALUES

Autoignition temperatures have been measured for numerous pure hydrocarbons, with most published data acquired using the standard ASTM E659 procedure [1]. The most extensive compilations of autoignition temperature data are those of Mullins [12], Zabetakis [11,13], McCracken [14], and the National Fire Protection Association [15]. Table 3 lists the values from the first two studies assembled by Glassman [18].

As mentioned in Section I, the standard ASTM procedure for measuring autoignition temperatures often involves extended times of several minutes. During this time there is ample opportunity for fuel decomposition, leading to autoignition of a complex mixture of hydrocarbons. In sharp contrast, in the present measurements the contact time of the hydrocarbon vapor and the heated metal surface is only ≈ 90 ms, in order to ensure that the measured temperature indicates the ignition of the original fuel. One anticipates, therefore, considerably higher autoignition temperatures will be observed under our experimental conditions. Indeed, this is found to be the case; compare Tables 1 and 3. We measure autoignition temperatures in the range of 655 - 1141 °C for the series of 15 hydrocarbon fuels impinging upon nickel, stainless steel, and titanium surfaces. In fact, as mentioned in Section III.B.5, the actual surface temperatures were 50 - 60 °C higher than our reported thermocouple values. The earlier results span a range of 218-632 °C for a quartz surface. There is no overlap in the data sets. The quartz surface employed in the ASTM procedure does not explain this difference. Pfefferle et al. [5,6] reported autoignition temperatures on quartz only about 110-135 °C less than they found on platinum for lean ethane/air mixtures, and Coward and Guest [4] found that platinum exhibited autoignition temperatures 100-150 °C higher than any other metal surface for a range of stoichiometric conditions. These results suggest that the autoignition temperatures observed for a given fuel should be roughly similar for quartz and non-catalytic metal surfaces.

Table 3 reveals a wide variation, often exceeding 250 °C, in the earlier autoignition temperature results for many hydrocarbon fuels. Thus, it is difficult to compare these earlier data with the present measurements. Figure 8 is a plot of the literature data and our observed values on a nickel surface for the straight-chain alkane series. The overall trend toward lower autoignition temperatures with increasing chain length (with ethane, C_2H_6 , being low) is similar for our results and for the highest reported autoignition temperatures. However, our temperature values are systematically higher by over 300 °C. Our data show no indication that autoignition temperatures may increase for hydrocarbons larger than C_8 molecules (see Reference 19 and papers cited therein). In general the present results indicate a small decrease in the measured autoignition temperature as the fuel/air mixture becomes richer (see Table 1). This is opposite the trend reported by Coward and Guest for a wide variety of metal surfaces [4].

Table 3. Literature Values of Autoignition Temperatures (°C);
from Glassman [18].

Methane	632, 537, 540
Ethane	472, 515
Ethylene	490, 543
Acetylene	305, 335
Propane	493, 450, 466, 504
Propylene	423
Butane	462, 543, 477
1-3 Butadiene	418
n-Pentane	579, 290, 284
n-Hexane	487, 520, 248, 261, 225, 261
Benzene	538 - 740 (from McCracken [14])
Cyclohexane	259, 270, 245
n-Heptane	451, 230, 233, 250, 247
n-Octane	458, 218, 240
iso-Octane	561, 434, 447, 515, 415

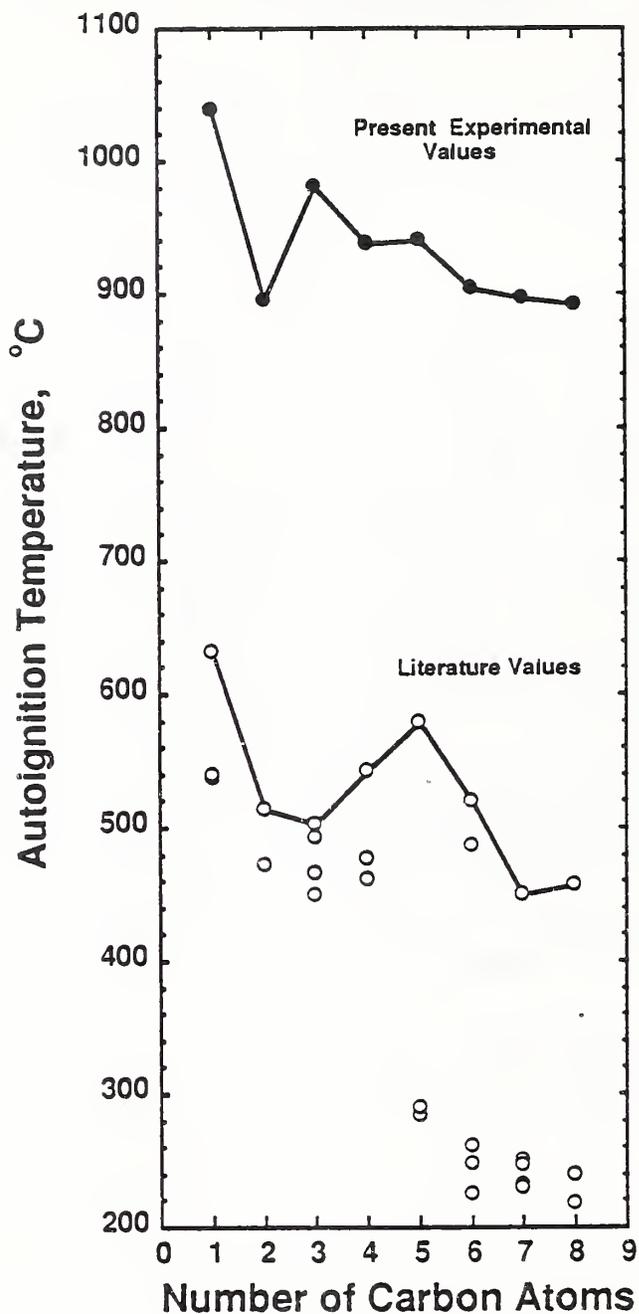
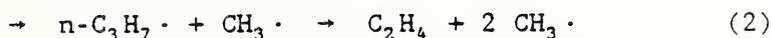
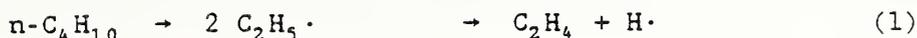


Figure 8. Comparison of Measured Autoignition Temperatures as a Function of Carbon Number for Linear Alkanes. Solid symbols: our measurements; open symbols: literature values taken from Glassman (18). Solid lines connect the results of the present study and the highest literature values.

SECTION VI DISCUSSION

A. RADICAL-BASED CHEMICAL MECHANISMS

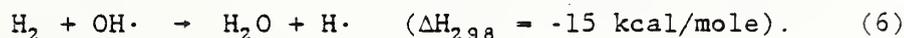
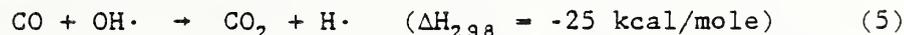
Autoignition, or spontaneous ignition, is usually considered to be controlled entirely by gas-phase reactions involving free radicals. The ignition behavior for hydrocarbons has been found to be critically dependent upon fuel structure [11-15,19,20]. Initially a hydrocarbon fuel pyrolyzes by thermally breaking the weakest carbon-carbon bond. Consider the case of n-butane decomposition as a typical example. Two routes leading to different alkyl radicals are possible [21]



Following this fuel breakdown process, the build-up of the radical pool concentrations ($\text{OH}\cdot$, $\text{H}\cdot$, and $\text{O}\cdot$) via chain-branching reactions such as



is essential for ignition to occur, since the main heat release reactions involve $\text{OH}\cdot$ [22],



For the ignition of n-butane, Reaction 1 leads directly to the production of H-atoms via the decomposition of the ethyl radical ($\text{C}_2\text{H}_5\cdot$) and thus to the chain-branching Reaction 4, whereas Reaction 2 eventually gives only the much less reactive methyl radical ($\text{CH}_3\cdot$). In this way the identity of the alkyl radicals formed initially by pyrolysis and their subsequent chemical reactions plays a key role. For such a radical-based mechanism for autoignition, it is evident that the autoignition behavior of hydrocarbon fuels is sensitive to any chemical process which leads to chain branching. The relative ease with which the radical pool concentrations build up will have a large influence upon the ease of autoignition.

However, the initial decomposition products alone do not determine the autoignition behavior of a hydrocarbon fuel. If this were the case, one would expect that ethane would exhibit a particularly high autoignition temperature, since breaking the weakest bond (C-C bond) leads exclusively to the formation of unreactive $\text{CH}_3\cdot$ radicals. However, our data show that ethane (and other C_2 hydrocarbons) are anomalously easy to ignite. The autoignition time involves the sum of the times for fuel decomposition, the production of intermediate hydrocarbons, and the oxidation of these intermediates to CO and H_2O [23]. Important factors include the site-specific abstraction of hydrogen atoms,

isomerization of the resulting alkyl radicals by internal H-atom abstraction, and rapid β -scission of the alkyl radicals. All of these processes affect the production of H atoms and in turn the radical pool concentrations [23]. In addition, the specific nature of the intermediate hydrocarbons is important. For example, electron rich species (such as allene and benzene) may inhibit autoignition due to electrophilic addition reactions with H·, O·, and OH·.

This complexity of numerous chemical processes has thus far precluded the formulation of a simple predictive model of the autoignition behavior for hydrocarbon fuels. Combustion product analysis studies have monitored a large number of intermediate products in the ignition of even relatively small hydrocarbons. As a result, extended chemical models have been proposed in order to explain autoignition behavior. For fuels such as heptane and iso-octane a comprehensive chemical mechanism has been developed which incorporates some 212 species and 1530 reactions [24] !

B. END-GAS AUTOIGNITION - ENGINE KNOCK

Since knock in spark-ignition engines is caused by end-gas autoignition, a large number of experimental and modelling studies on the autoignition of hydrocarbons have been carried out to better understand knock processes. Fuel structure effects are also observed to be of particular importance [25], and the time for autoignition has been found to be a monotonic function of the Research Octane Number (RON) in investigations of engine knock [24] (RON is a measure of knock susceptibility in internal combustion engines, where higher numbers imply slower ignition times). End gas conditions for autoignition involve high pressures (20 - 30 atm) and temperatures in the range of 225-825 °C. The end gas typically experiences a rapid change in temperature (approximately 500 °C) within 40 ms - not unlike the experimental conditions in the present study. At higher pressures an additional route for radical chain branching becomes increasingly important [26]:



In their recent study of n-butane and isobutane combustion Wilk et al. [27] also concluded that the isomerization reactions of $\text{RO}_2\cdot$ radicals are important for chain branching in the case of n-butane. In contrast, for isobutane chain branching depends upon $\text{HO}_2\cdot$ reactions, which occur at higher temperatures and lead to the observed higher Research Octane Number.

Various modelling approaches have been attempted in order to describe the intermediate temperature and high pressure conditions of engine knock. These include empirical relations, comprehensive kinetic models (as the example cited above), and models which include only rate-limiting reactions [28]. The predictions of reduced chemical kinetic mechanisms with detailed mechanisms have been compared for the combustion of n-pentane and iso-octane [29]. For such intermediate size hydrocarbon fuels, autoignition has been described in terms of degenerate chain branching, a negative temperature coefficient

region, and a two-stage ignition process [22,28,30]. Despite the different pressure regime, many of the chemical models used to describe engine knock are based upon experimental studies of hydrocarbon oxidation carried out at atmospheric pressure and at temperatures of 425-725 °C [21,23,30-32]. Models developed from these investigations have then been extended to the conditions appropriate for engine knock. Temperature effects are found to be much more important than the influence of varying pressure [26]. Both these experiments and the modelling descriptions of engine knock can be informative in trying to predict the autoignition behavior of hydrocarbons.

In his study of n-heptane oxidation at atmospheric pressure, Morley [30] has discussed the key chemical stages as follows:

- (1) $T > 725$ °C: alkyl radicals decompose and H-atom reactions dominate;
- (2) $T = 575-725$ °C: $\text{HO}_2\cdot$ abstraction and H_2O_2 decomposition processes are significant; and
- (3) $T < 575$ °C: peroxy radicals ($\text{RO}_2\cdot$) control the chemistry.

The earlier models of hydrocarbon oxidation emphasized high-temperature processes and concluded that the low-temperature reactions had no effect upon the calculated autoignition times for end-gas conditions [22,23,26,32]. More recently, however, it has been recognized that this description is oversimplified [24] and that "even if the actual autoignition occurs at high temperatures, the reactions taking place at low temperatures play a very important role in governing whether or not it will occur by generating heat and intermediate products" [30]. Since autoignition does not occur until the fuel is consumed [24], all of the oxidation kinetics in the 225-725 °C region must be included. A key question which is not resolved at present is whether the low-temperature chemical reactions (1) act to form intermediate hydrocarbons which pre-condition the gas mixture and subsequently lead to autoignition or (2) whether they simply provide sufficient heat to initiate high temperature autoignition processes [33].

No simple predictive model or straightforward approach has yet been developed for calculating autoignition behavior as a function of fuel type for hydrocarbons. Some insight does emerge on the expected role of stoichiometry for gas phase autoignition, although the calculated autoignition times [34] and the measured shock tube ignition delay times [35] depend in a complex manner upon temperature, pressure, and stoichiometry. Smith et al. [26] predict that the autoignition temperature of a hydrocarbon fuel should decrease slightly for richer conditions, due to the role of low temperature chemical reactions (additional fuel leads to more H_2O_2 and thus further chain branching via Reaction 8). However, Lifshitz et al. [36] point out that hydrocarbon fuels are expected to inhibit their own ignition. The prediction of Smith et al. [26] agrees with our experimental findings, which show a small decrease in the measured autoignition temperature of most hydrocarbons for rich conditions (see Table 1). In terms of fuel structure effects, for conditions of $\phi = 0.5-1.5$ (i.e., fuel lean to fuel rich) Pitz and Westbrook

[22] found no change in the ranking of radical + fuel reactions for a number of hydrocarbons.

In the combustion literature on the knocking tendencies of hydrocarbons the early compilation of Lovell [25] stands out as an excellent summary of observed fuel structure effects; the data are presented in terms of the measured critical compression ratio required for knock to occur. In addition, the following observations concerning fuel structure effects upon autoignition times have been explained in terms of specific chemical steps. For comparison with our experimental temperature measurements, shorter times should correlate with lower autoignition temperatures.

1. Straight-chain hydrocarbons < branched chain molecules [21]; octane < iso-octane [23], also found in experimental measurements of shock tube ignition delay times [37]. Our data are limited to a comparison of iso-octane and n-octane; iso-octane is found to be more resistant to autoignition, as expected.
2. Laminar flame speed faster for propylene than for propane [38]; propylene more reactive than propane for $T > 375$ °C [39]. In contrast, we observe generally higher autoignition temperatures for propylene.
3. N-butane < iso-butane < propane; similar to trend for critical compression ratios [26]; Research Octane Number: butane < iso-butane < propane; quoted in Pitz and Westbrook [22]. In agreement, we observe generally lower autoignition temperatures for n-butane than for propane (the nickel surface is an exception).
4. Acetylene < ethane < ethylene < methane - calculated by Lutz et al. [40]. In general agreement, we find that autoignition temperatures for these fuels lie in the order acetylene < ethylene < ethane < methane.
5. Alkane isomers can often be ranked with the critical compression ratio by the relative production of iso-butene [31]. We have insufficient data to comment on this point.

SECTION VII RECOMMENDATIONS FOR FUTURE WORK

The following areas are fruitful for the further investigation of fuel structure and surface effects on autoignition temperatures and their interpretation in terms of detailed chemical mechanisms:

A. LINEAR CHAIN VERSUS BRANCHED CHAIN HYDROCARBONS

The knock literature, both experimental measurements and modelling studies, strongly indicates that autoignition temperatures should be higher for branched chain hydrocarbons than for the corresponding linear isomers. Our limited data (iso-octane and octane) support this analysis for all three of the metal surfaces which we investigated. Further studies along these lines could be carried out easily with the existing apparatus. Specifically, autoignition temperature data are needed on the series iso-butane, iso-pentane, branched hexanes, ... in order to ascertain whether or not branched chain hydrocarbons would reduce autoignition hazards.

B. FUEL MIXTURES

Thus far we have investigated the ignition behavior of single hydrocarbon fuels and have focussed our attention on fuel structure effects. Mixtures of these simple hydrocarbons can be studied to ascertain the applicability of additivity rules for the prediction of ignition temperatures for mixtures. In particular, binary mixtures of hydrocarbon fuels from different classes (i.e., alkanes, alkenes, and aromatics) can be investigated to probe for unusual synergistic effects. Some recent measurements of the autoignition temperature for binary mixtures have been reported using the standard ASTM procedures [41]. Data on fuel mixtures would aid developing a capability to predict the autoignition temperatures of complex hydrocarbon blends, such as Mil H-5606 hydraulic fluid, Mil H-83282 hydraulic fluid, Mil-L-7808 lubrication fluid, JP-4,5,8, and kerosene. The effect of specific fuel additives upon autoignition temperatures can also be measured.

Current experiments on liquid fuels utilize a bubbler arrangement to introduce the fuel into the gas phase. To prevent fractional distillation of the lighter component in a fuel mixture, atomization procedures would need to be developed.

C. ALLOYS AND NON-METAL SURFACES

Our present apparatus is designed to measure autoignition temperatures near a hot metal foil. Additional simple metal surfaces can be investigated, such as platinum, gold, bronze, monel, and carbon steel, as well as alloys used in the aircraft industry (aluminum/magnesium/titanium). Also of interest are non-metal surfaces, which include ceramics, quartz, and composite materials (graphite, carbon fiber). Various surface coatings and preparations, such as sandblasting and pickling, can also be investigated.

Our present apparatus employs DC current to heat the metal foil to the desired temperatures by means of electrical resistance. Non-conductive surfaces will require indirect heating. The design and testing of such an approach may involve significant time and effort.

D. UNEXPLAINED PHENOMENA

We have observed two interesting phenomena which warrant further study:

1. The addition of small amounts of water to ethylene/air mixtures significantly lowers the autoignition temperature in the presence of a hot nickel surface. Is this true in general for all hydrocarbon fuels? Are radicals such as H-atoms and OH· being produced in abundance near the hot surface?

2. Red spot ignition. For rich ethylene/air mixtures a seemingly autocatalytic ignition occurs. At sufficiently high temperatures (but well below the autoignition temperature by ≈ 150 °C) a red spot appears on the nickel surface. Further heating of the foil is not necessary, as its temperature continues to rise until ignition. How general is this phenomenon for metal (and non-metal) surfaces as well as other fuel/air mixtures?

E. DETAILED CHEMICAL MECHANISMS

Our test apparatus has been designed to provide facile access for optical and mass spectrometric experiments. Considerable insight into the chemical mechanisms most important in autoignition can be gained by making radical profile measurements using laser techniques (such as laser-induced fluorescence and multiphoton ionization) and probing stable species with a mass spectrometer. What are the important gas phase species? Are critical radical concentrations required in the gas phase, irrespective of the hot surface? Are typical combustion products, such as water and carbon dioxide, detectable before ignition occurs - for example in the "red spot" ignition phenomenon?

Optical and mass spectrometric measurements may well provide the most direct means for testing specific autoignition reaction mechanisms after a temperature database has been established. Such data would also help us begin to understand the phenomenon of hot spark ignition.

Using the same experimental arrangement as in the present investigation, quartz microprobe mass spectrometric sampling of CO₂ and H₂O near the heated metal surfaces can be carried out [42]. In addition this apparatus can be combined with a pulsed dye laser and optical system suitable for the excitation and detection of the OH·, H·, and O· radicals. We have performed similar measurements in atmospheric pressure diffusion flames [43], while Pfefferle et al. report data obtained near heated metal surfaces [5,6].

SECTION VIII
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A new apparatus has been designed, built, and extensively tested for making short-duration autoignition temperature measurements of hydrocarbon fuels under conditions where the fuel/air stoichiometry, the nature of the hot metal surface, and the contact time are well controlled. This approach provides a much more reliable database to establish the importance of fuel structure effects than the current ASTM E659 procedure. Over 1100 individual autoignition temperature determinations have been made for the ignition of 15 hydrocarbon fuels on heated nickel, stainless steel, and titanium surfaces for three different fuel/air mixtures (0.7, 1.0, and 1.3). Excellent reproducibility has been achieved with the new apparatus. The measured autoignition temperatures generally decrease for the larger hydrocarbons and the richer mixtures, with C₂ hydrocarbons (ethane, ethylene, and acetylene) having particularly low values. The highest autoignition temperatures are observed for nickel surfaces and the lowest for stainless steel, with titanium being an intermediate case. A review of the autoignition literature suggest that the branched alkanes should be more resistant to autoignition than the linear isomers, and thus present a reduced hazard. Limited data obtained in this study are consistent with this prediction. Promising directions for substantiating these observations and additional areas for future research are outlined.

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